Light Scattering Techniques for Polymer Materials

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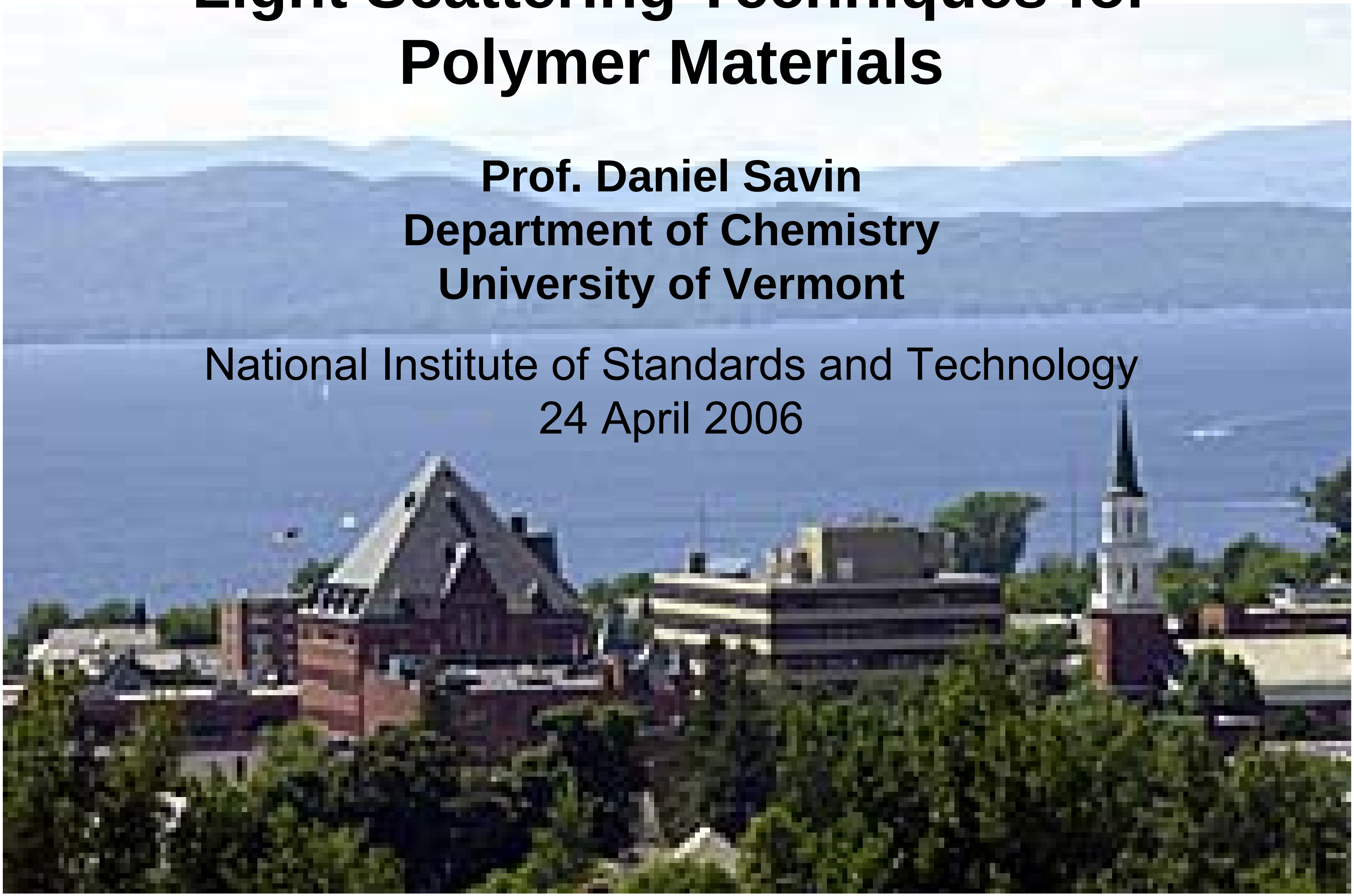
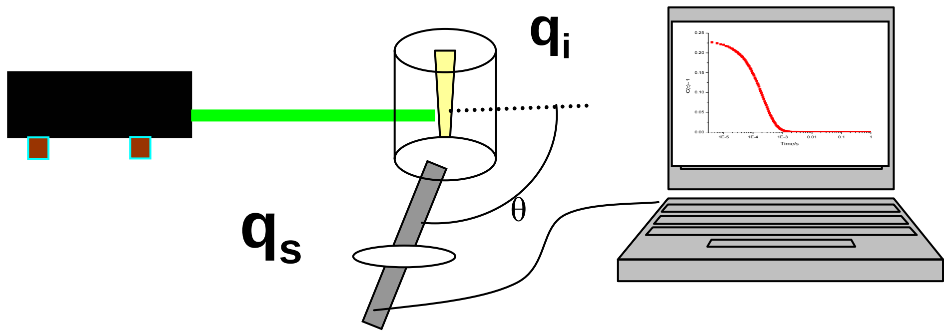
24 April 2006

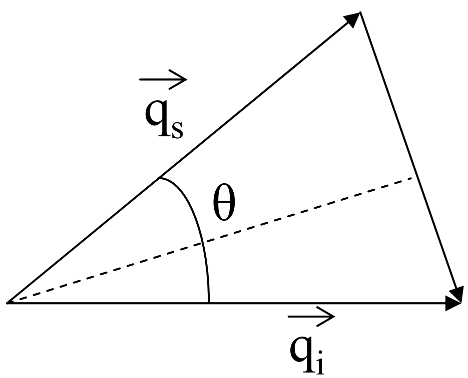


Overview

- Brief description of light scattering formalism and experiments
- Applications to the solution behavior of responsive block copolymer assemblies

Experimental Setup





Scattering vector:

$$\mathbf{q} = \mathbf{q}_s - \mathbf{q}_i$$

$$q = |\mathbf{q}| = \frac{4\pi n}{\lambda}\sin\left(\frac{\theta}{2}\right)$$

Light is scattered by local fluctuations in the medium

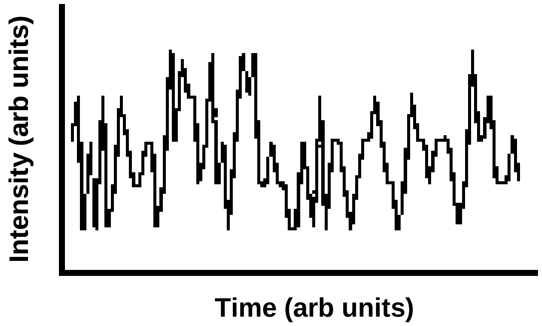
Considerations

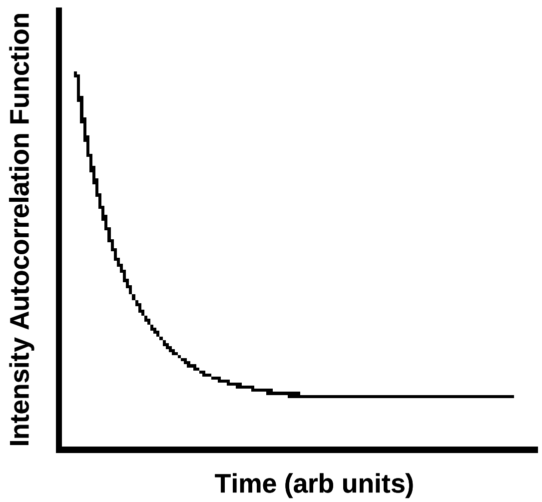
- Where do local fluctuations come from?
  - Density
  - Concentration
  - Osmotic pressure
  - Longitudinal (phonon propagation)
  - Orientation
- Timescale - dynamic vs. static
- Lengthscale relative to q

Dynamic Light Scattering

- Commonly used for particle sizing in dilute solution
- Key technique for the characterization of small-molecule and polymeric surfactants, as well as micelles that are responsive to solution conditions
- **Measure time dependence of the scattered intensity via an autocorrelation function**

Correlation Functions





Berne and Pecora, Dynamic Light Scattering, 1976, Dover.

- For diffusion, the relaxation time is on the order of tenths of milliseconds

Intensity vs. time looks like noise.

If the time between samples is on the same time scale of the dynamics, then the intensities are **correlated**.

$$g^{(2)}(\tau) = \frac{\langle I(t+\tau)I(t)\rangle}{\langle I\rangle^2} = 1 + F(A)\left[g^{(1)}(\tau)\right]^2$$

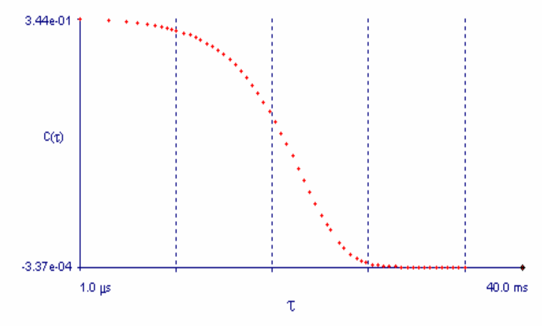
Contains dynamic information!

$$g^{(1)}(\tau) = e^{-\Gamma\tau} \qquad \Gamma = D_M q^2$$

For diffusive motion:
Plot Γ vs. q^2:
Slope equal to D_m

Decay function analysis (I)

Method of Cumulants:



Assume narrow, unimodal distribution:

$$g^{(1)}(\tau) = \sum_{i=1}^{n} G(\Gamma_i)\exp(-\Gamma_i \tau_i)$$

$$\ln g^{(1)}(\tau) = \left[\ln g^{(1)}(0)\right] - \langle\Gamma\rangle t + \frac{\mu_2}{2!}t^2 - \frac{\mu_3}{3!}t^3 + \frac{\left(\mu_4 + 3\mu_2^2\right)}{4!}t^4$$

$$\langle\Gamma\rangle = \langle D_M \rangle q^2$$

$$pdi = \frac{\mu_2}{\langle\Gamma\rangle^2}$$

Normalized Variance

$$\langle D_m \rangle \approx \langle D_o \rangle = \frac{kT}{6\pi\eta\langle R_h \rangle}$$

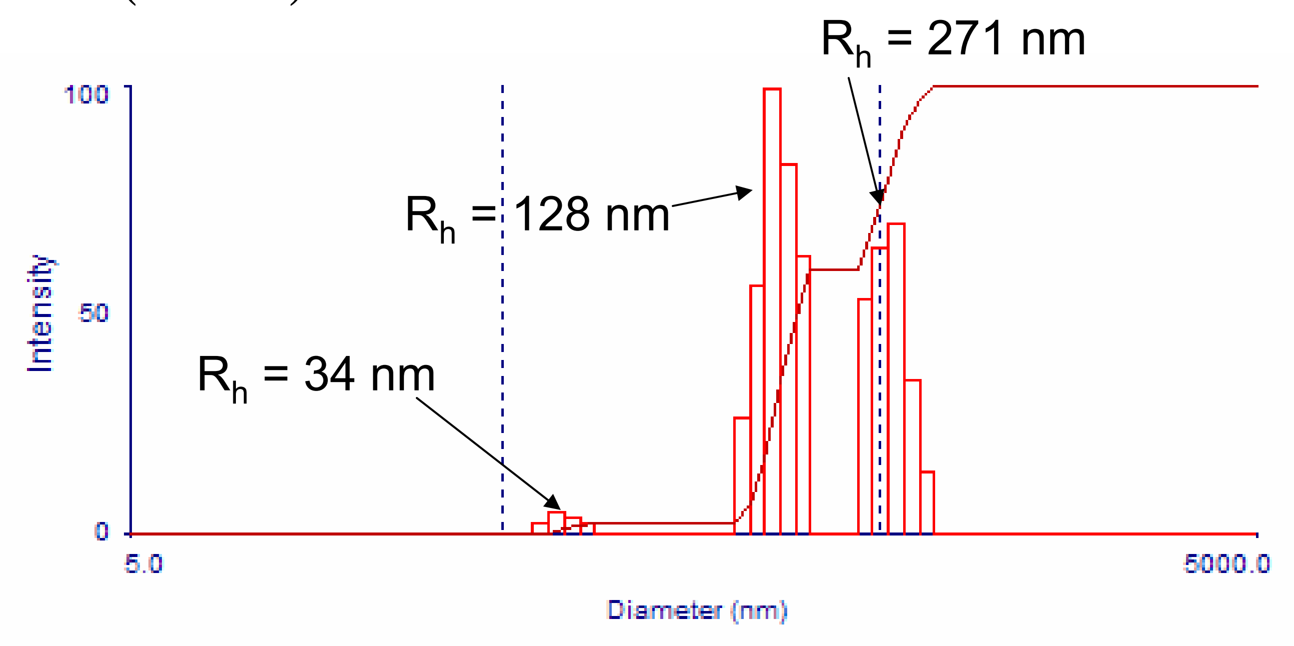
Want pdi < 0.3

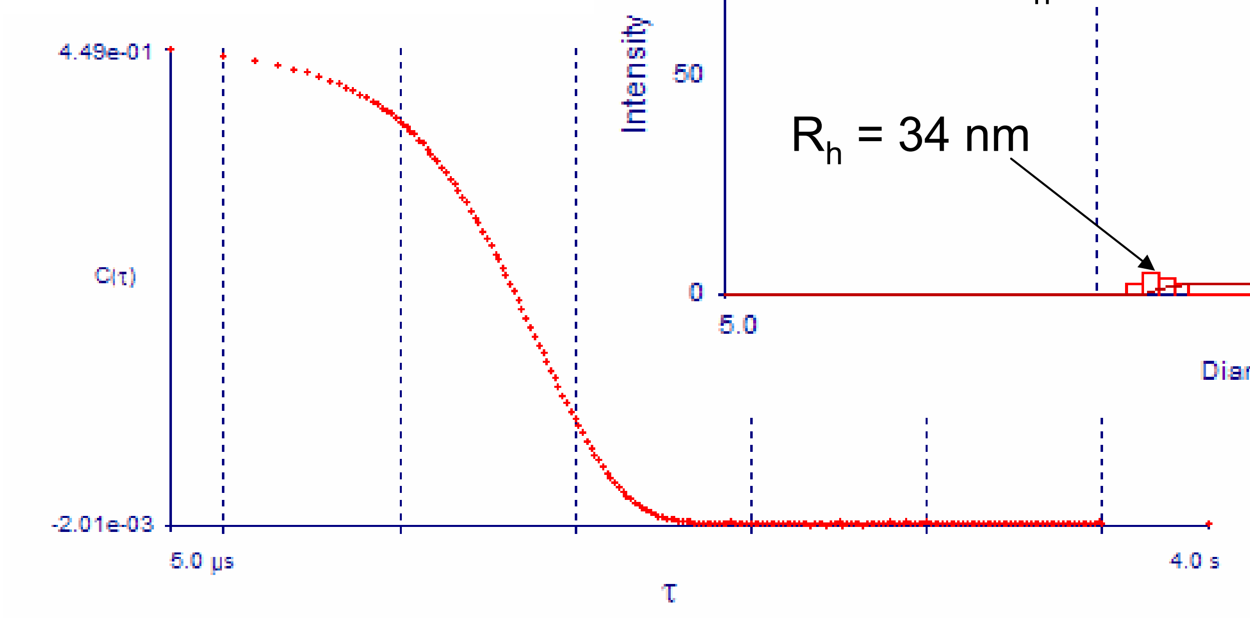
Decay Function Analysis (II)

Model the decay as a distribution of relaxation rates

$$g^{(1)}(\tau) = \sum_{i=1}^{n} G(\Gamma_i)\exp(-\Gamma_i \tau_i)$$

PB-PEO vesicles





NNLS or CONTIN Analysis

Depolarized DLS

- Measure the intensity of scattered light polarized perpendicularly to the incident light:

Now:

$$g^{(1)}(\tau) = e^{-\left(D_m q^2 + 6\theta\right)\tau}$$

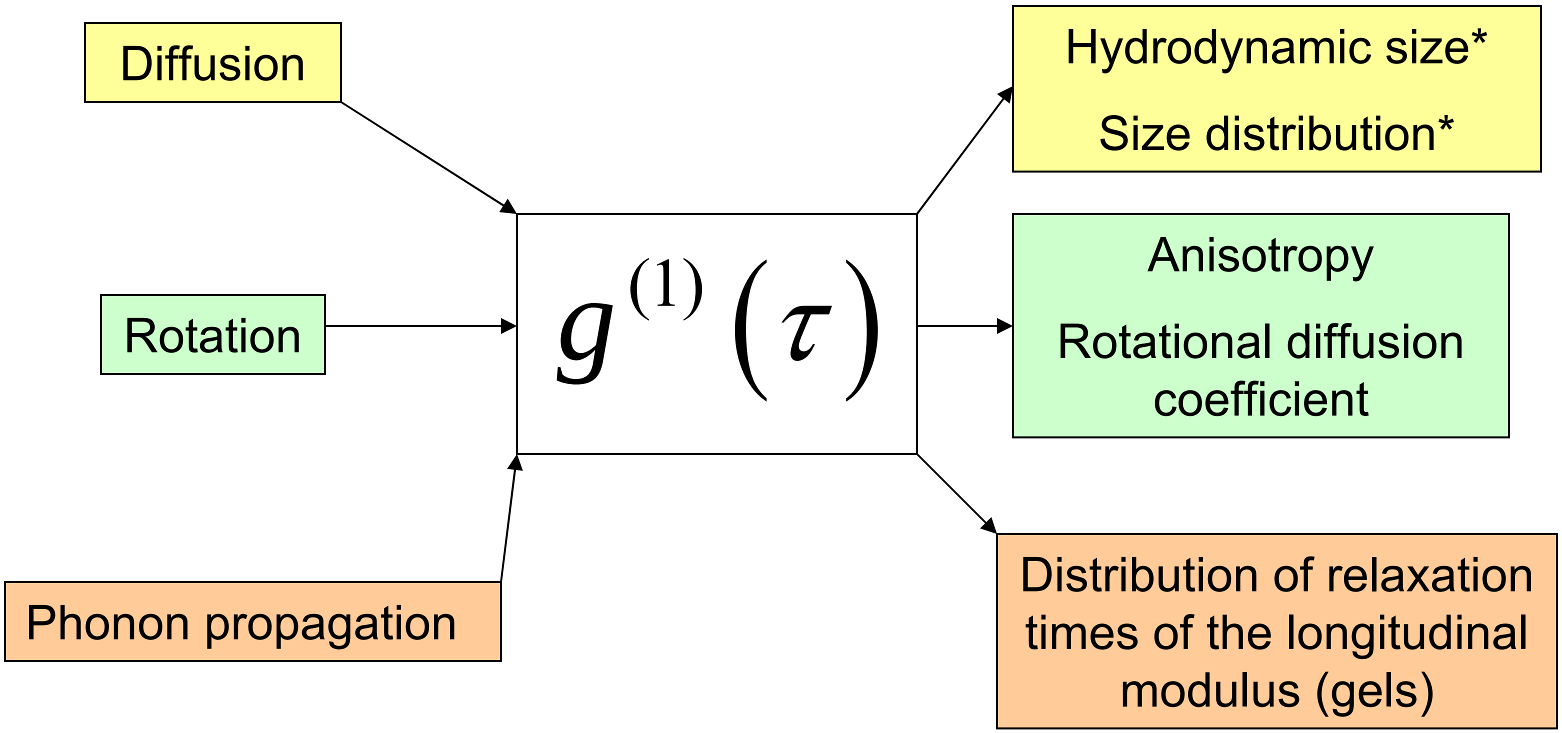
and:

$$\theta = \frac{kT}{8\pi\eta R^3}$$ Is the rotational diffusion coefficient.

Note the stronger R dependence, but spherical molecules have zero depolarized intensity

By incorporating shape dependences into D and θ , you can extract a size and axial ratio of the particle

Relaxation Functions in DLS



Static Light Scattering

- Measure the time averaged scattering intensity
- Osmotic fluctuations come about from solution thermodynamics
- Obtain information about weight averaged molecular weight, size, shape and solution thermodynamics
- **Applications**: M_w determination of homopolymers, CMC and aggregation number determination of micelles, shape analysis

SLS Formalism

Based on the Zimm equation:

$$\frac{Kc}{R_\theta} = \frac{1}{M_w P(q)} + 2A_2 c + \ldots$$

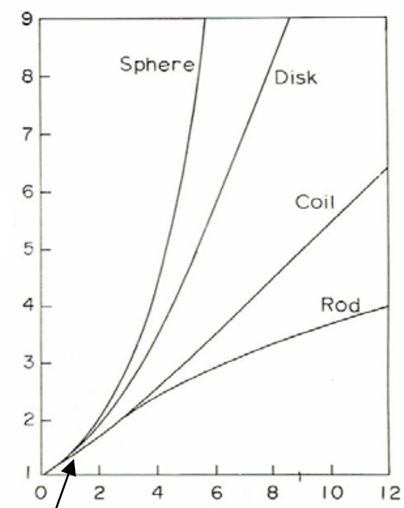
$$K = \frac{4\pi^2 n^2 (\partial n/\partial c)_0^{\,2}}{\lambda_0^{\,4} N_A}$$

$$P(q) = \left[\frac{3}{(qR)^3} \left(\sin qR - qR\cos qR \right) \right]^2$$

Form factor for sphere

A_2 is the second osmotic virial coefficient

$P^{-1}(q)$



$q^2R_g^{\,2}$

$$P(q) = 1 - \frac{(qR_g)^2}{3} + \ldots$$

For qR <<1

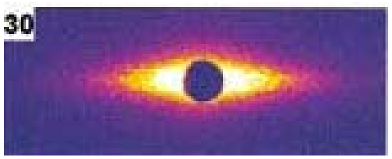
Small Angle Light Scattering

- SALS is another type of (depolarized) SLS experiment
- Similar formalism to SAXS/SANS
  - Fit intensity data to obtain P(q)
  - Relate to distance distribution function
- **Since q range is much larger than SAXS/SANS, SALS works best for large (~1-10 μm) particles**
- **Applications** – droplet formation, large vesicle characterization (ie: Norman *et al*.), phase separated polymers

Rheo-SALS and Birefringence

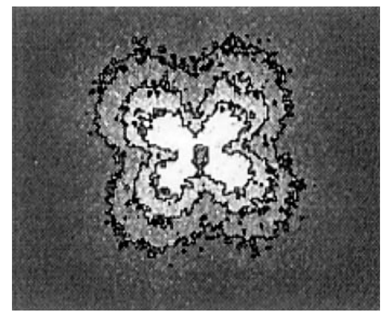
- Incorporating rheology (or flow birefringence) into the SALS experiment:

Bicontinuous Microemulsions



The bright streak is caused by elongated structures aligned in the direction of the flow, above a critical shear stress

Shear-induced vesicle formation from lamellar surfactant



Scattering is a result of concentration fluctuations that moderately couple to the flow

* From Krishnan, *et al*. *Phys. Rev. Let*. 2001, 098301

** From Schmidt, *et al. Rheol. Acta*. 1999, 486

In both experiments, the fluctuations are long ranged (on the order of microns)

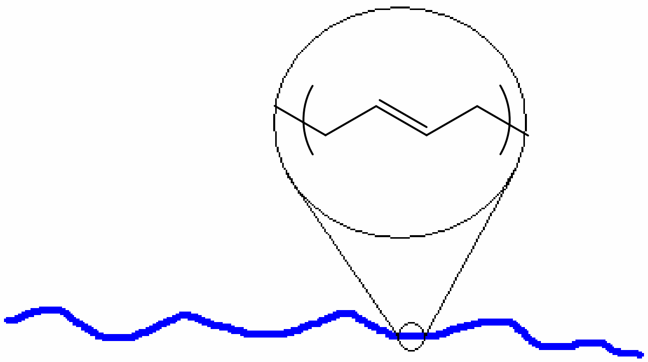
Light Scattering in Practice

- The Savin group is primarily interested in the solution characterization of pH and temperature-responsive block copolymer assemblies

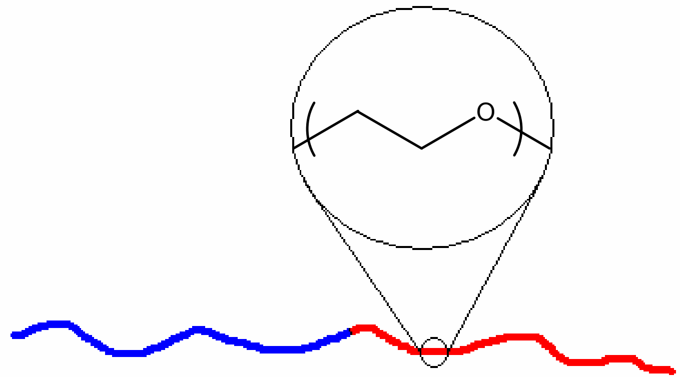
- **Techniques include:**
  - DLS to determine R_h
  - SLS (Kratky plots) to determine qualitative shape
  - Couple with TEM, rheology and other spectroscopic techniques

Applications of Light Scattering to Block Copolymer Assembly

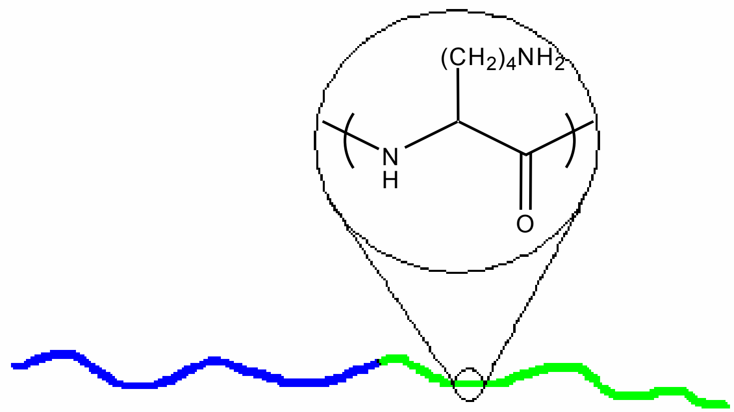
$1B market for
block copolymers



Poly(1,4 butadiene)
homopolymer



AB Diblock

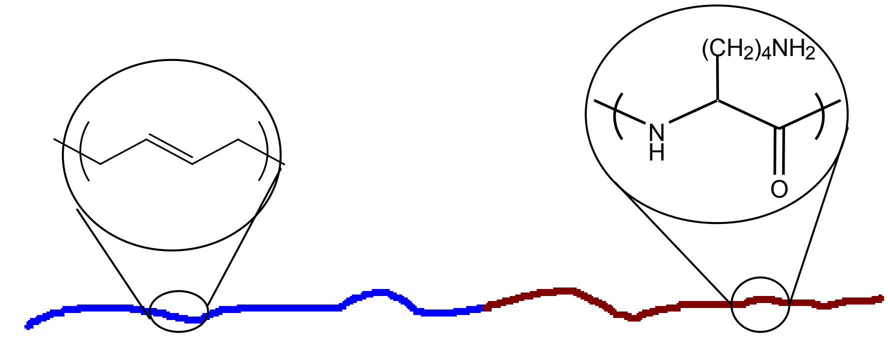


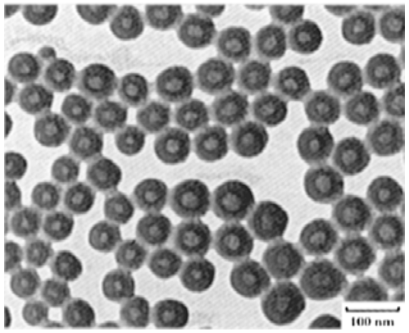
AC Diblock

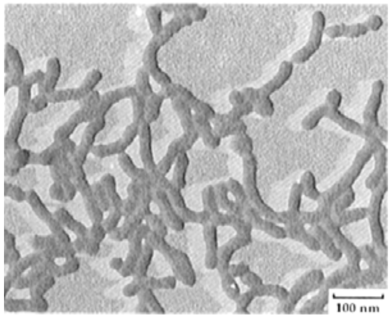
What happens when the blocks are not thermodynamically compatible?

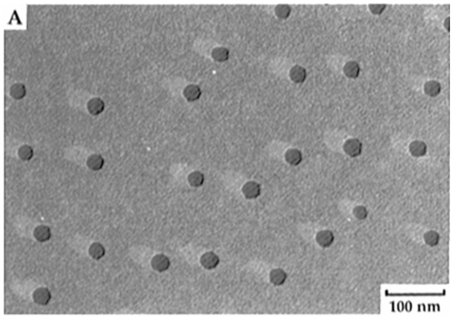
Self-Assembly

Solution Morphologies of Amphiphilic Block Copolymers









Vesicles
($f < 0.33$)

Wormlike micelles
($0.33 < f < 0.55$)

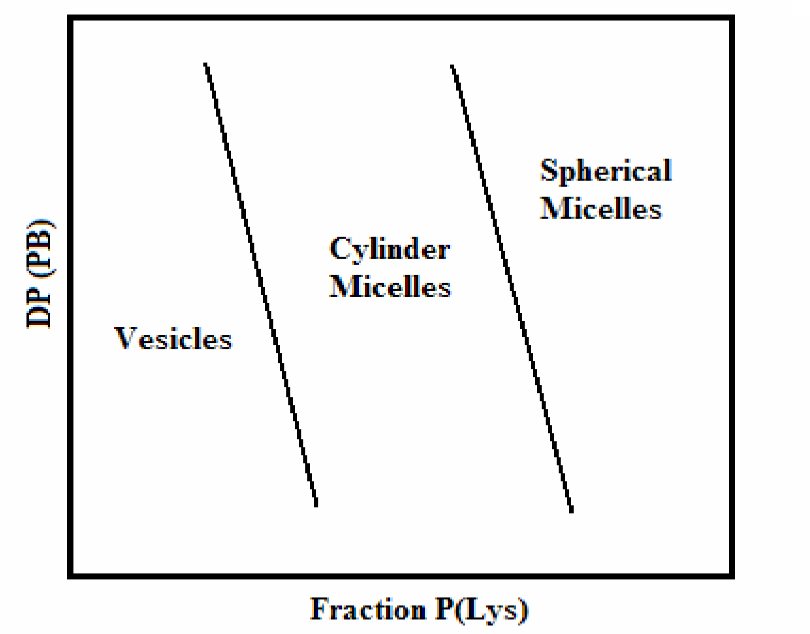
Spherical micelles
($f > 0.55$)

Increasing fraction of hydrophilic block →

*TEM Images from Zhang and Eisenberg. *J. Am. Chem. Soc.* **1996**, 118, 3168.

**PS PAA assemblies from 2% DMF solution

Phase Behavior of Amphiphilic Block Copolymers



- 'Phase diagram' of 1,4-PB-P(Lys)

Morphology dictated by:

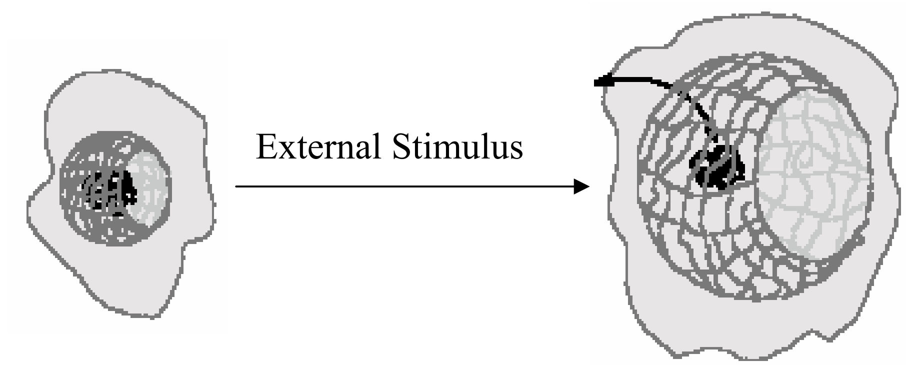
(1) Core chain stretching

(2) Corona chain crowding

(3) Surface tension

Stimuli Responsive Structures

Question: By changing the pH or temperature of a solution, can we disrupt the balance between thermodynamic parameters to induce changes in aggregate structure?



From Checot, *et al.* *Angew. Chem. Int. Ed*. **2002**, 1340.

Answer: YES!

3 things can happen:

(1) Aggregate swells – stretching of core and/or corona chains

(2) Destruction – surface tension can no longer hold aggregate together

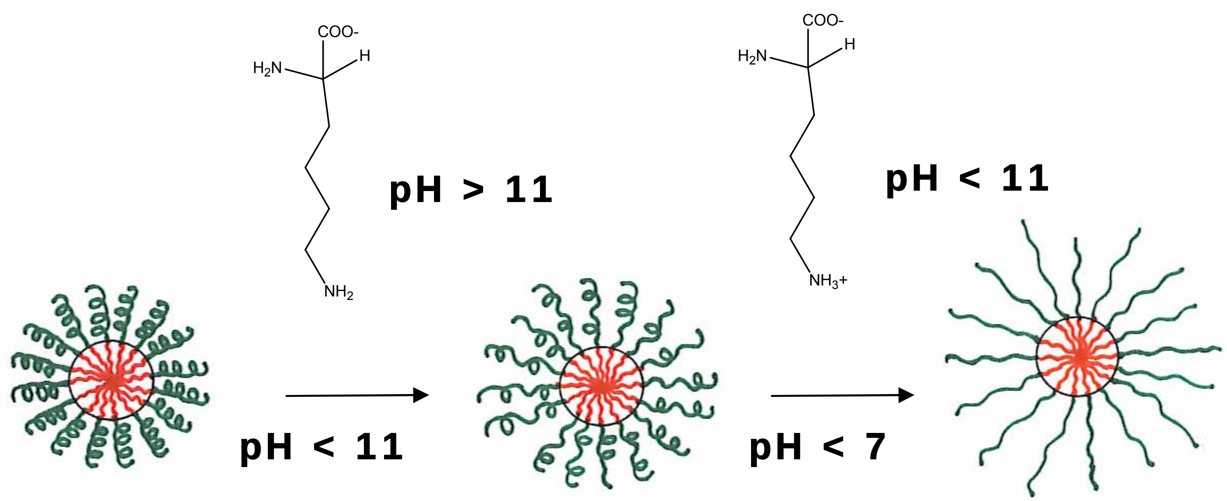
(3) Morphology shifts – crowding leads to dramatic curvature shift… Maybe?

Applications: Delivery, tunable viscosity, 'smart' materials

Current Directions

Target Molecule: PB-P(Lys)

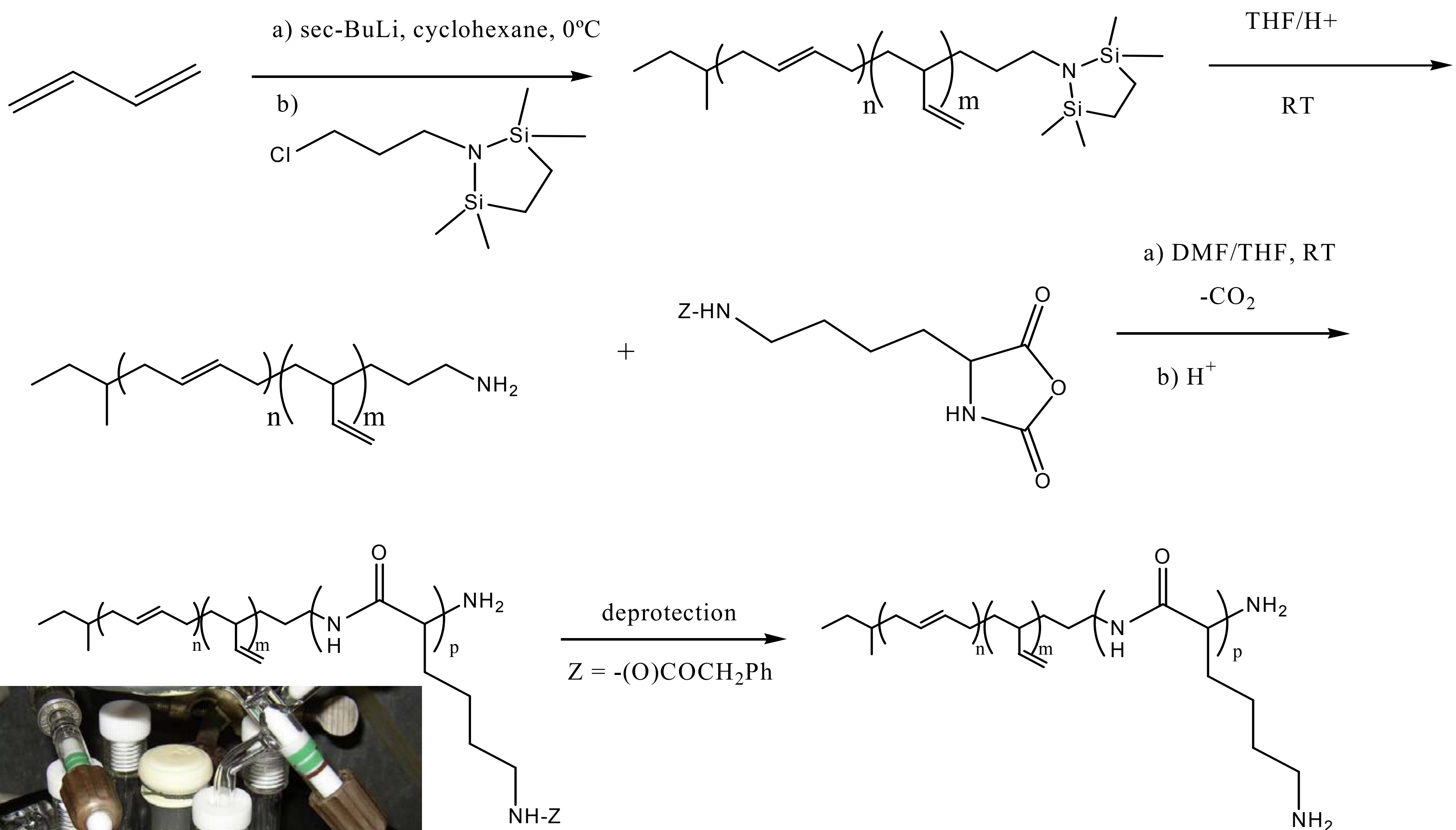
- At high pH, the side chains of poly(L-Lysine) are deprotonated and the polymer assumes an α-helical or a β-sheet conformation.
- At physiological pH, the side chains are protonated, resulting in an expanded coil configuration.
- Expansion of the poly(L-Lysine) α-helices results in swelling of the aggregate.



Advantages Over 'Traditional' Polyelectrolytes (PEs)

- Polypeptide-based block copolymers switch between rod-coil and coil-coil
- With PEs, modest change in solution dimensions from protonation/deprotonation
- With polypeptides, there is chain extension from both breaking the tight α-helical structure as well as directionality of pepide bond – not a true random coil structure

Synthesis of PB-P(Lys)



Ueda, K., Hirao, A. and Nakahama, S. *Macromolecules* **1990**, 23, 939-945.
Babin, J. *et al., Faraday Discuss*. **2005**, 128, 179-192.

**** Characterize with DLS, TEM**

pH Response of Deprotected Samples

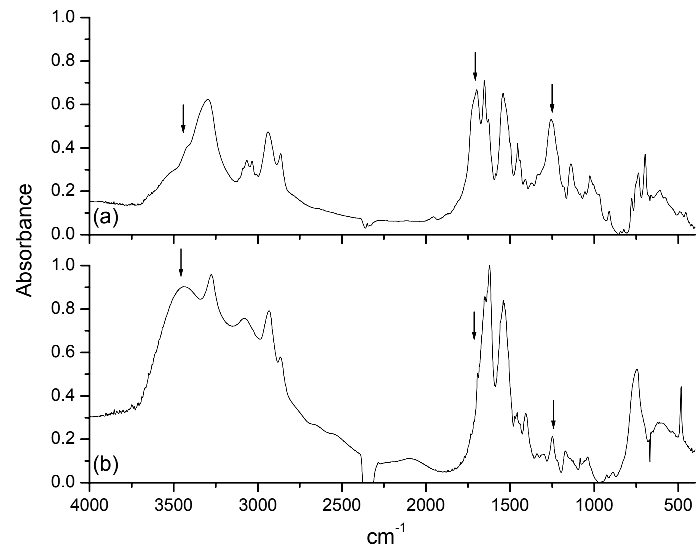
- Deprotection schemes:
  - HBr, catalytic hydrogenation
  - **HF cleavage**
- Efficient deprotection, leaving the unsaturation intact

pH Response for Low P(Lys) Fractions

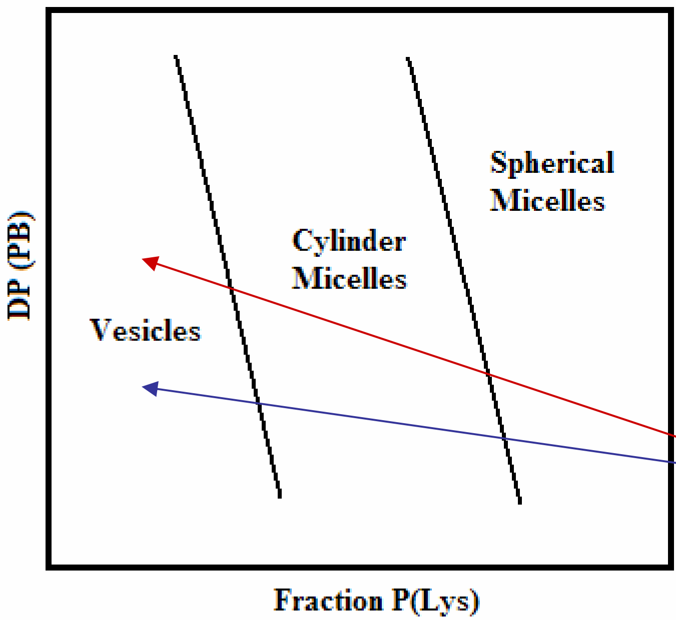
Compositions:

PB_{107}-$P(Lys)_{27}$

PB_{60}-$P(Lys)_{13}$

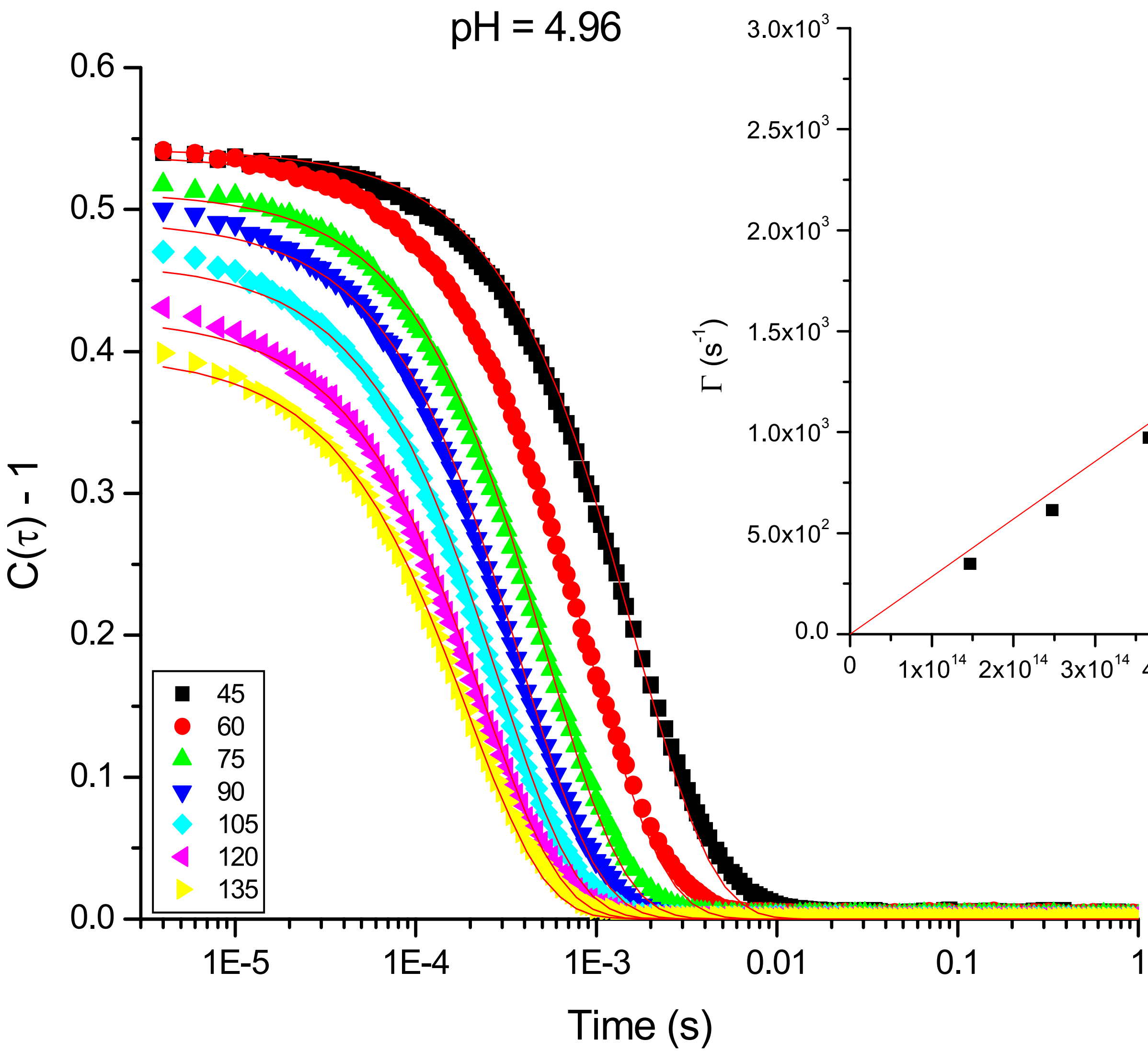


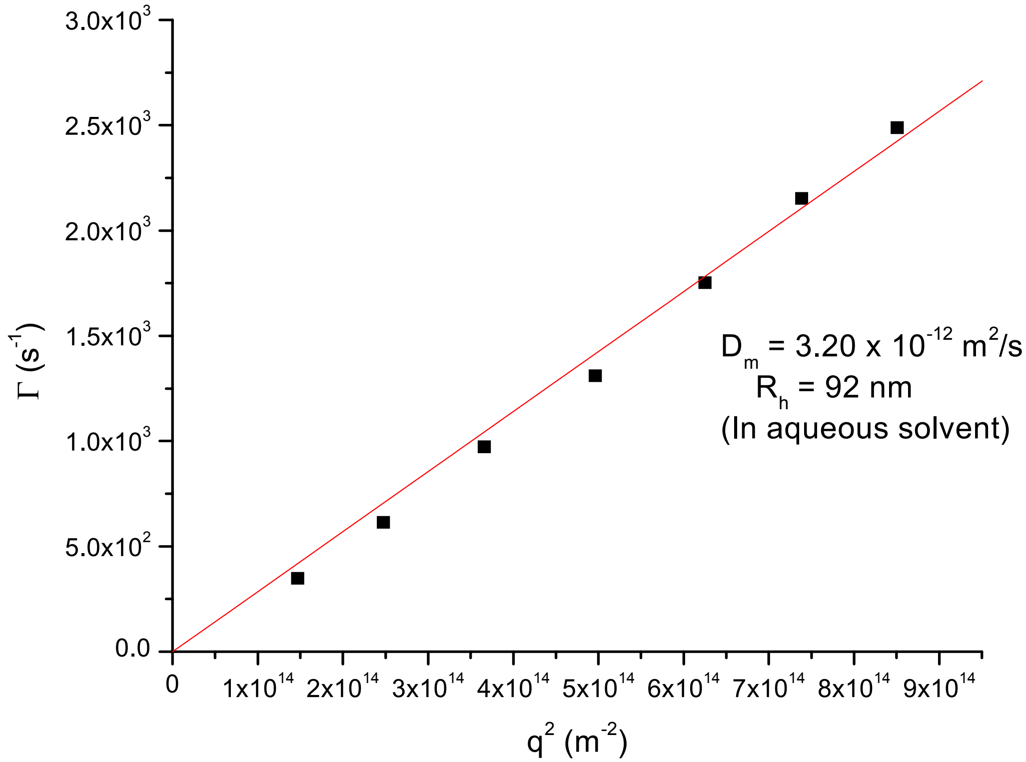
FTIR of protected (a) and deprotected (b) PB_{107}-$P(Lys)_{27}$



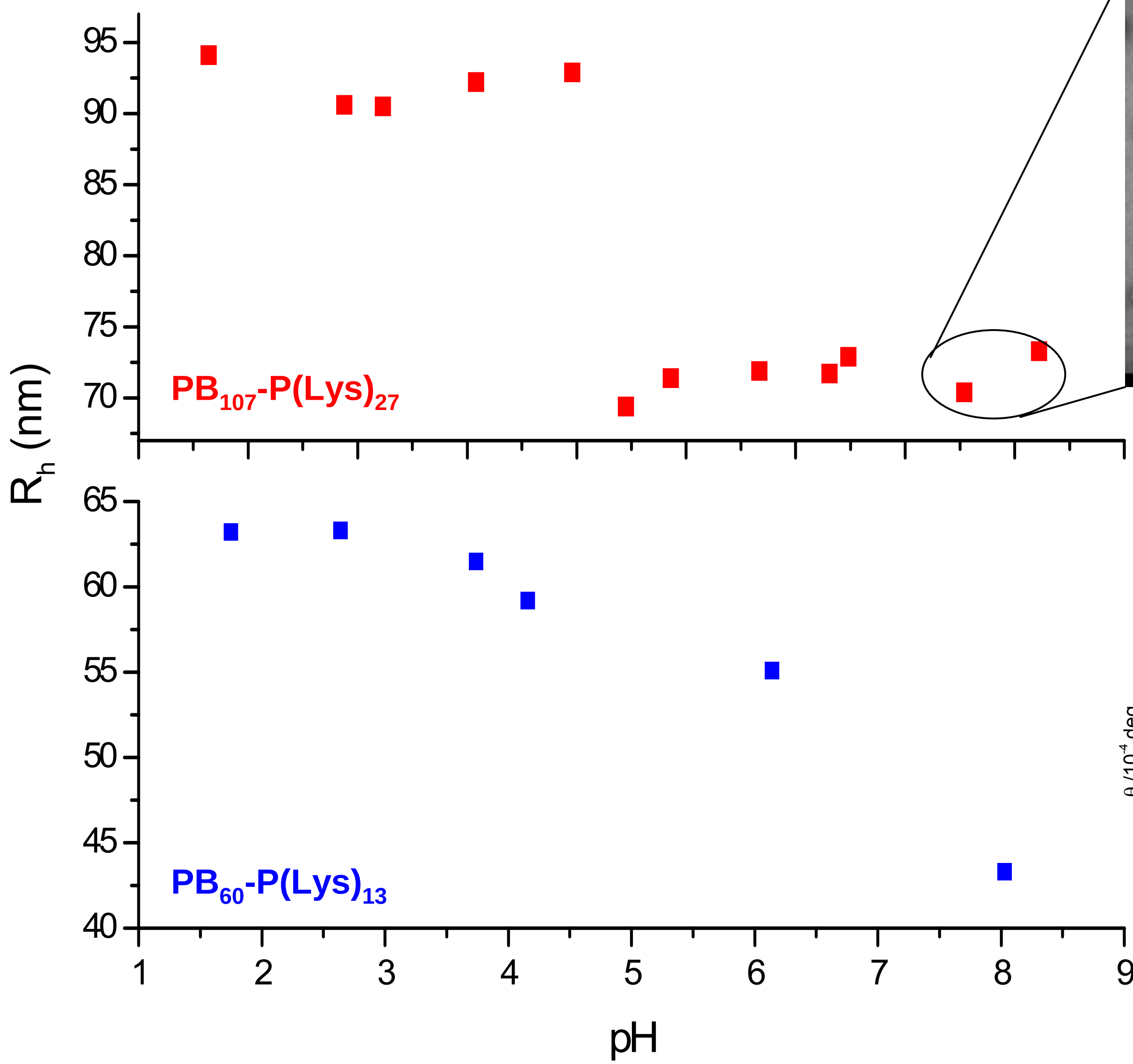
* Expect bilayer morphology

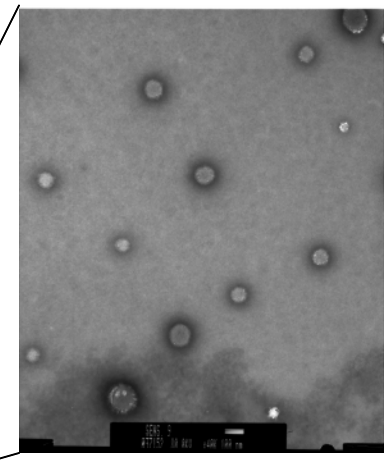
D_m of PB_{107}-$P(Lys)_{27}$





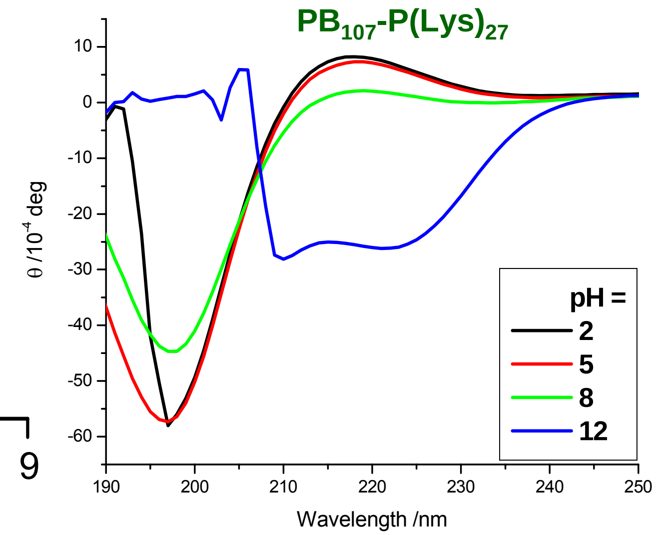
pH Response of PB_m-$P(Lys)_n$ from DLS



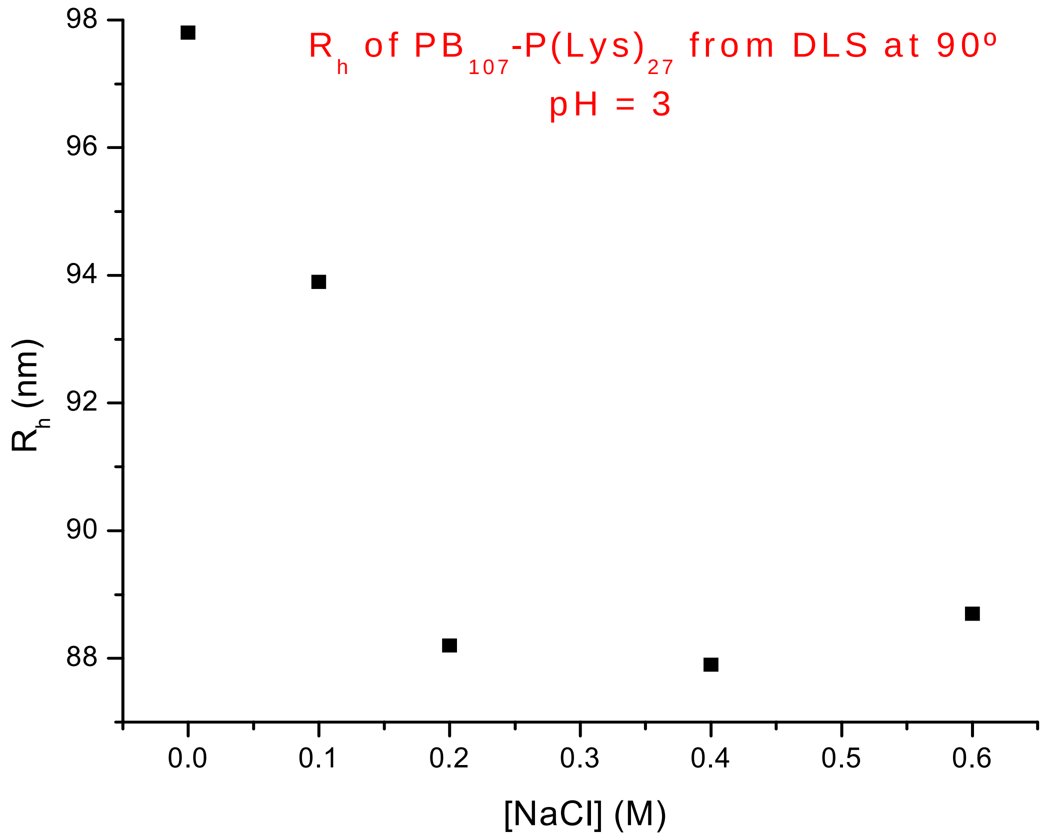


PB_{107}-$P(Lys)_{27}$
(scale = 100nm)

Circular Dichroism

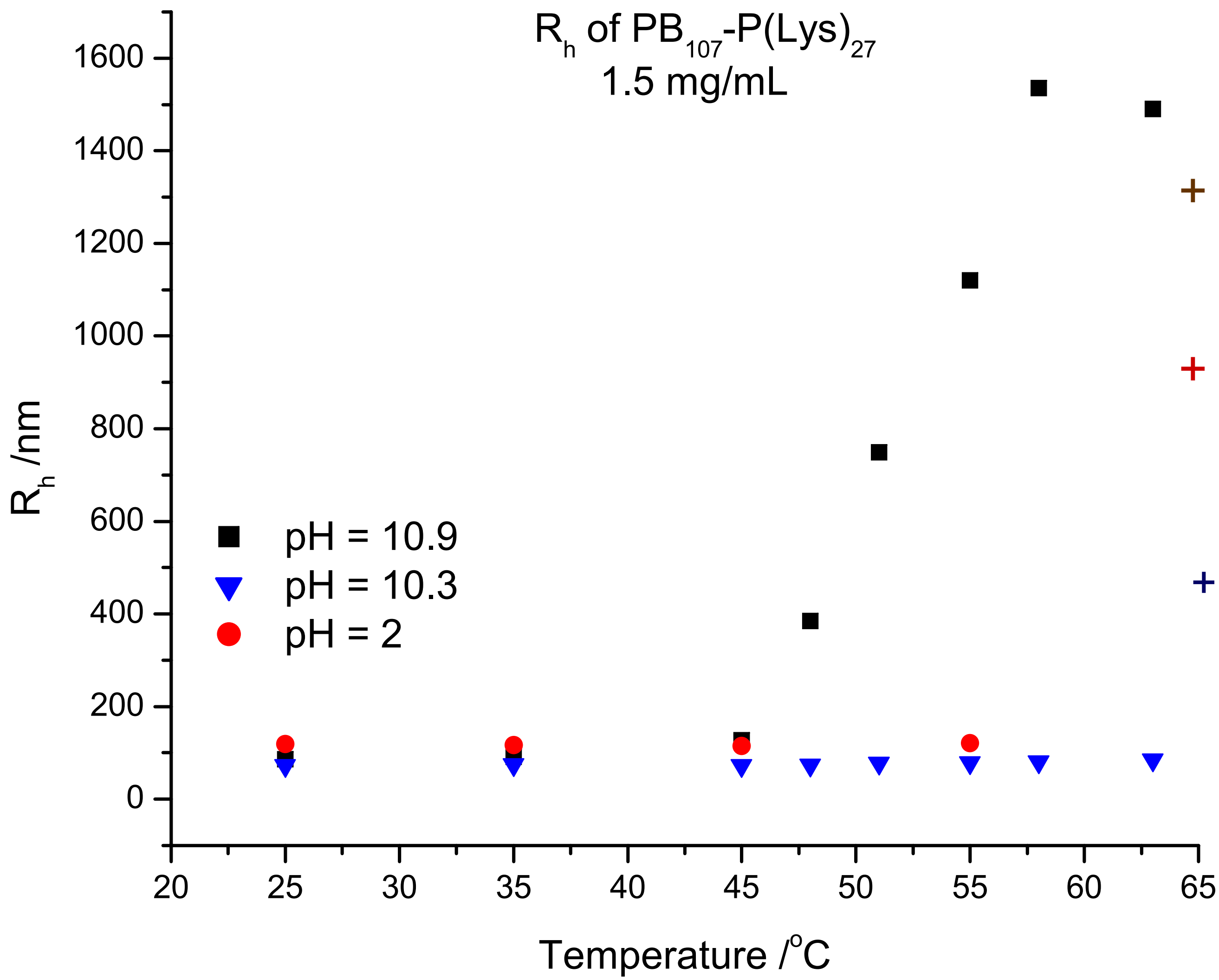


Effect of Ionic Strength



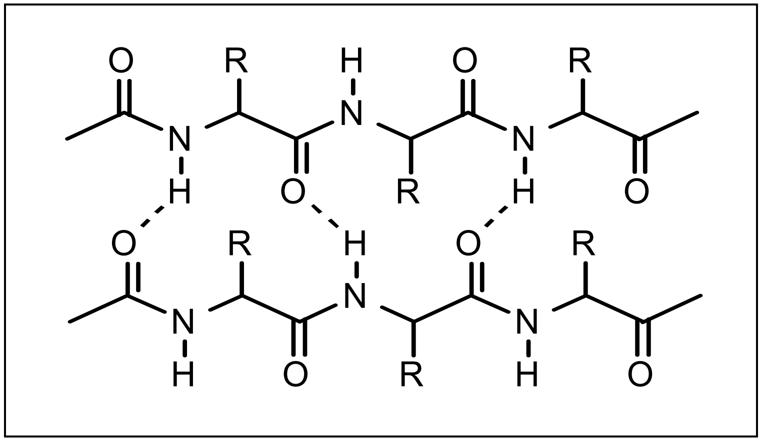
As [NaCl] increases, the size of the vesicles decreases as expected

Effect of Temperature

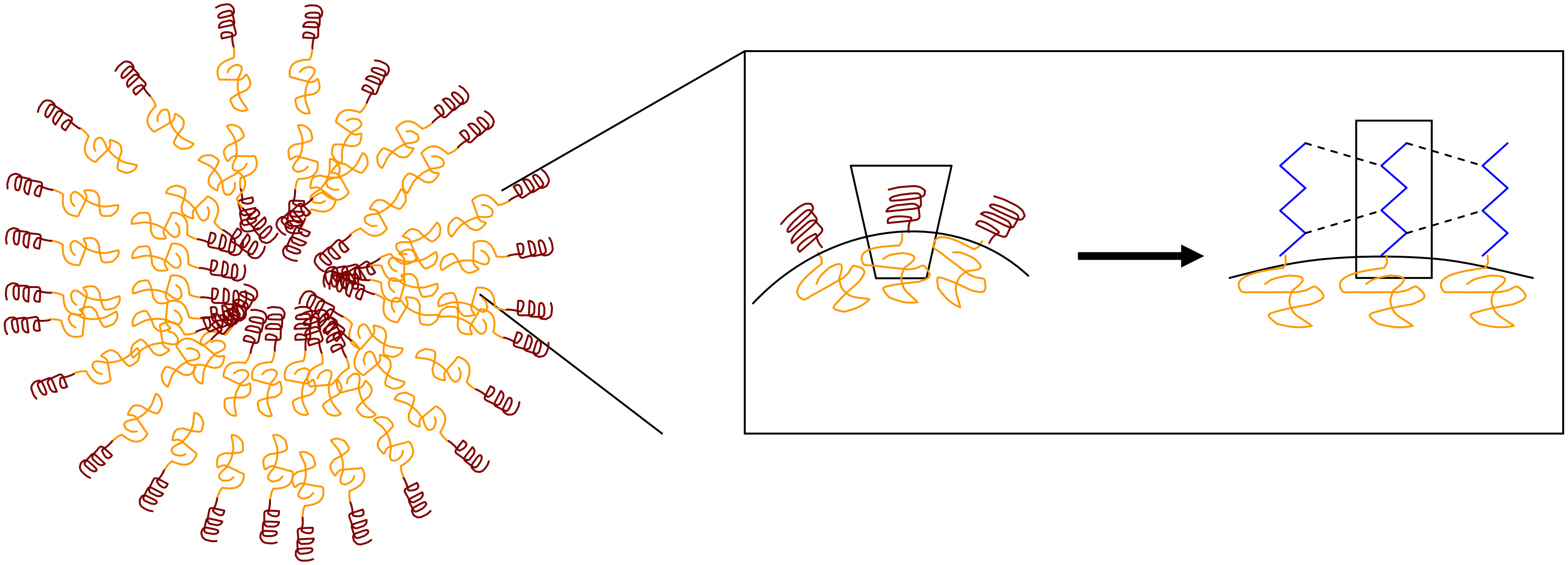


- Aggregates remain soluble
- 'Locally' irreversible, but retains character with addition of H^+
- Corresponds to helix-sheet transition temperature in P(Lys)

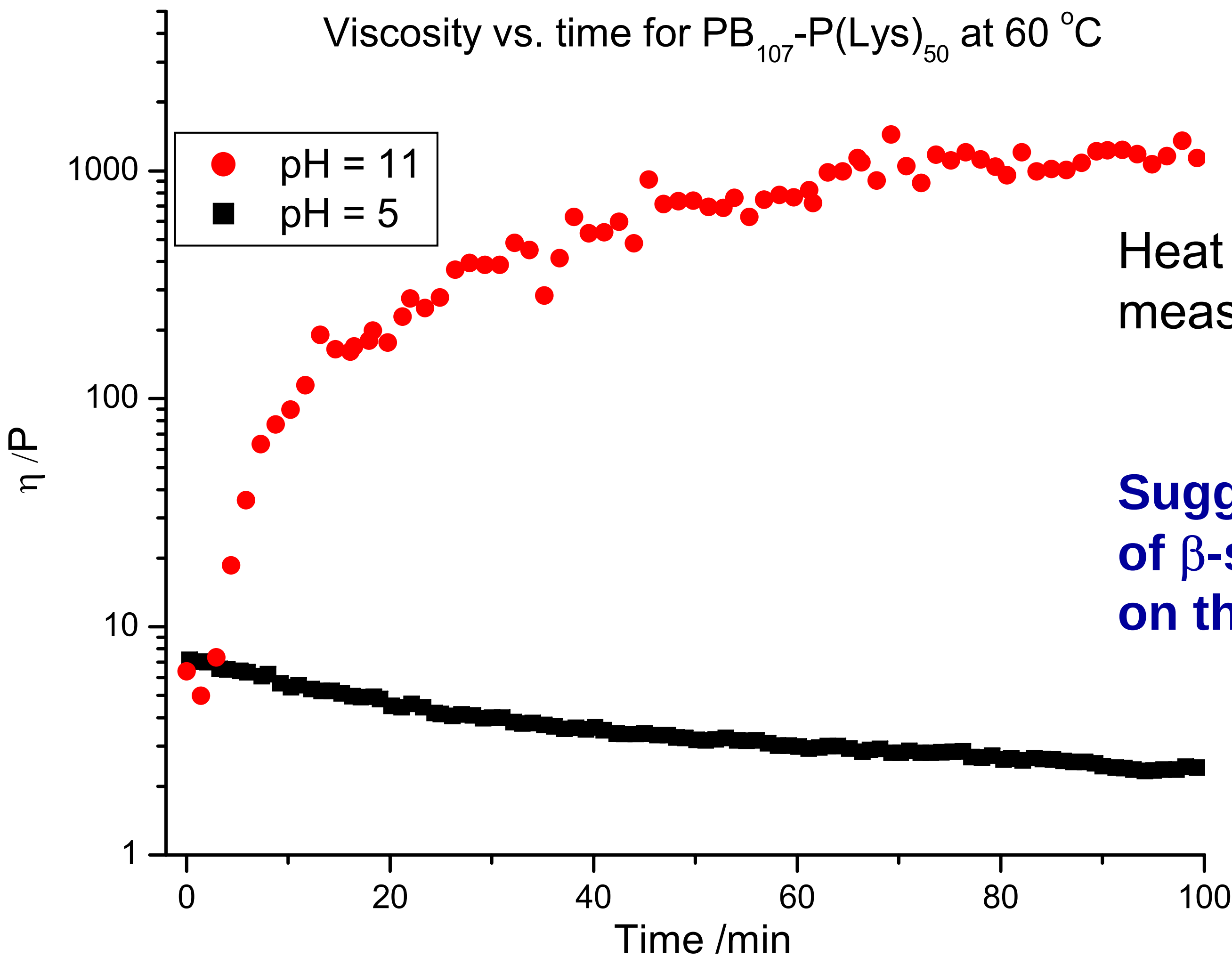
Intermolecular β-sheet Formation?



Parallel β-sheet formation within corona chains would cause a flattening of the interfacial curvature



Viscosity Enhancement at High T



Heat sample to 60 °C, measure viscosity vs. time

Suggests the time scale of β-sheet formation is on the order of 60 min

pH Response for Low P(Lys) Fraction

- pH response suggests vesicles are swelling at low pH. **This response is reversible**.
- CD confirms α-helical secondary structure at high pH, random coil at low pH
- Increase in vesicle size ~ 35%
- A decrease in the Debye length results in a decrease in vesicle size at low pH
- PB_{60}-$P(Lys)_{13}$ has limited solubility at high pH

Temperature Response for Low P(Lys) Fraction

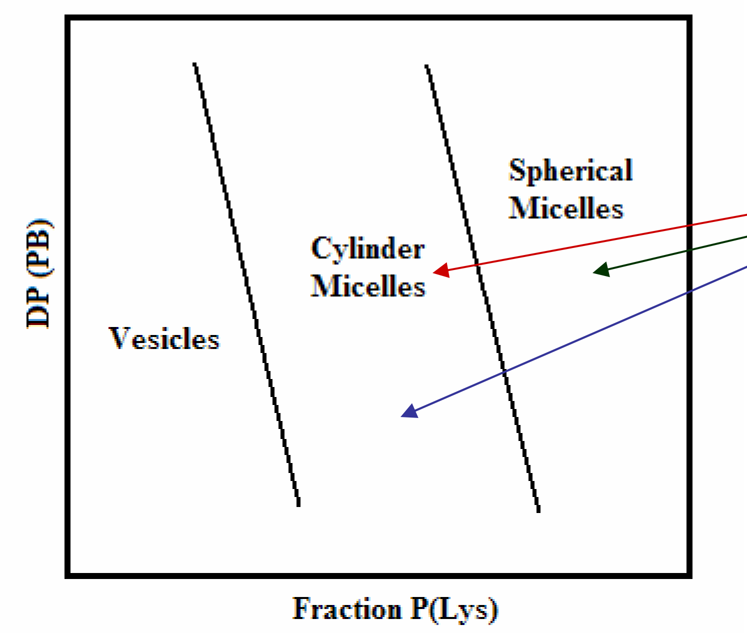
- As the temperature in increased at high pH, the aggregates in solution exhibit a dramatic increase in size and corresponding increase in solution viscosity
- This is potentially due to interchain β-sheet formation, which flattens the interfacial curvature of the assembly
- This change occurs over a very narrow pH range
- The timescale of the change is on the order of 60 min
- ‘Local’ irreversibility implies that there is a local minimum in the free energy with the b-sheet

pH Response for Higher Fraction of P(Lys)

Compositions:

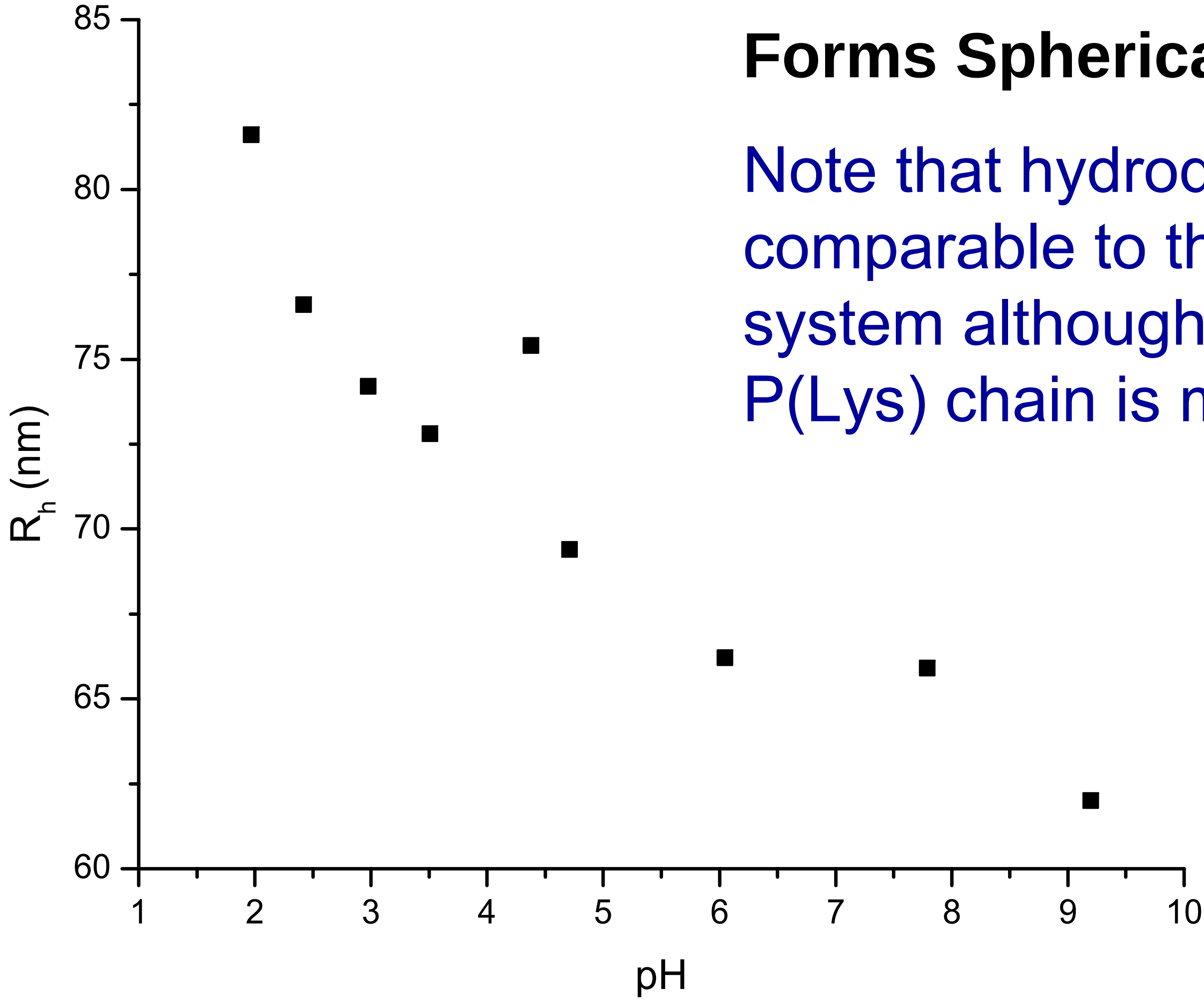
PB_{107}-$P(Lys)_{100}$ **PB_{107}-$P(Lys)_{200}$**

PB_{60}-$P(Lys)_{50}$



* Expect ?? morphology

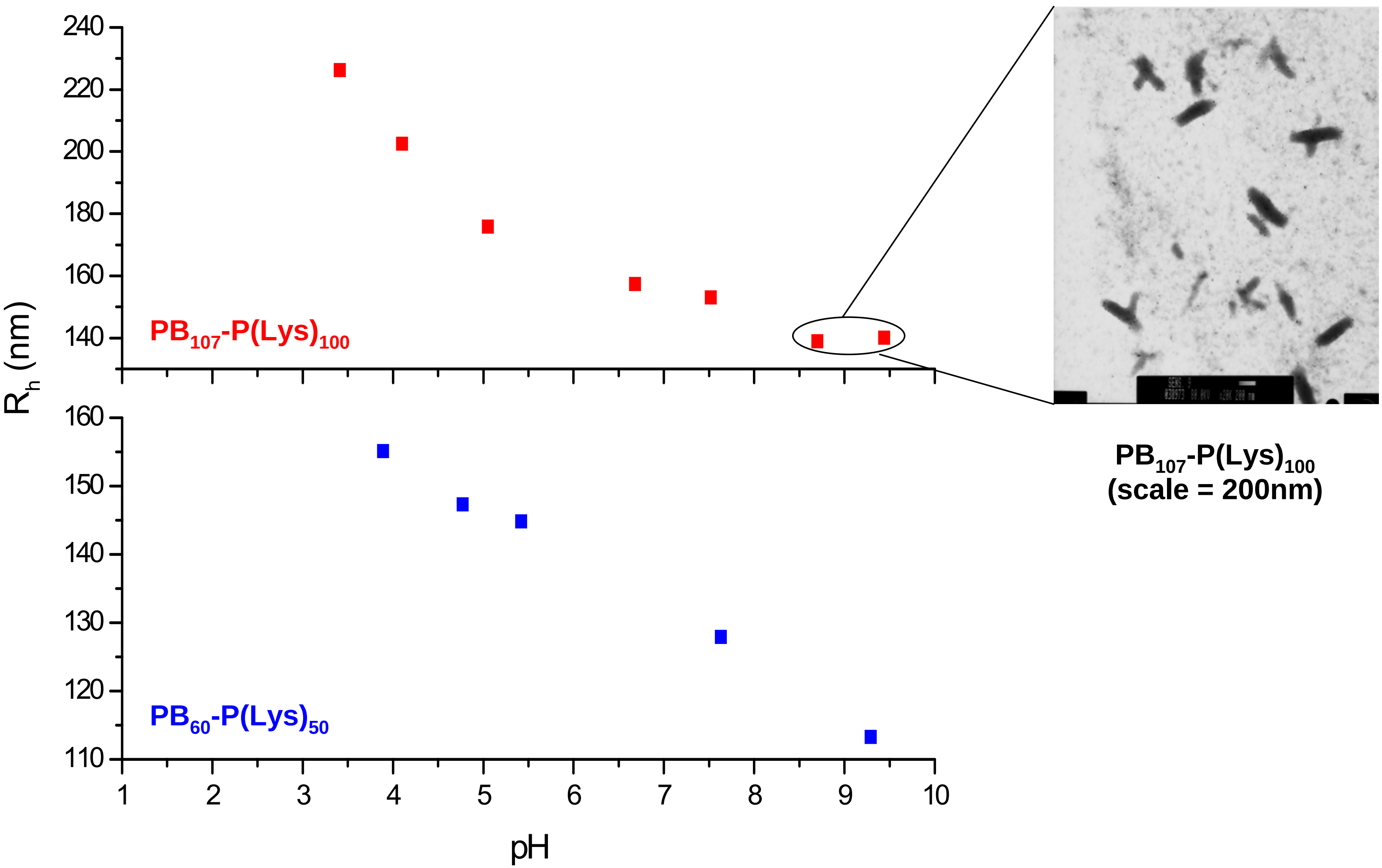
pH Response of PB_{107}-$P(Lys)_{200}$ from DLS



Forms Spherical Micelles:

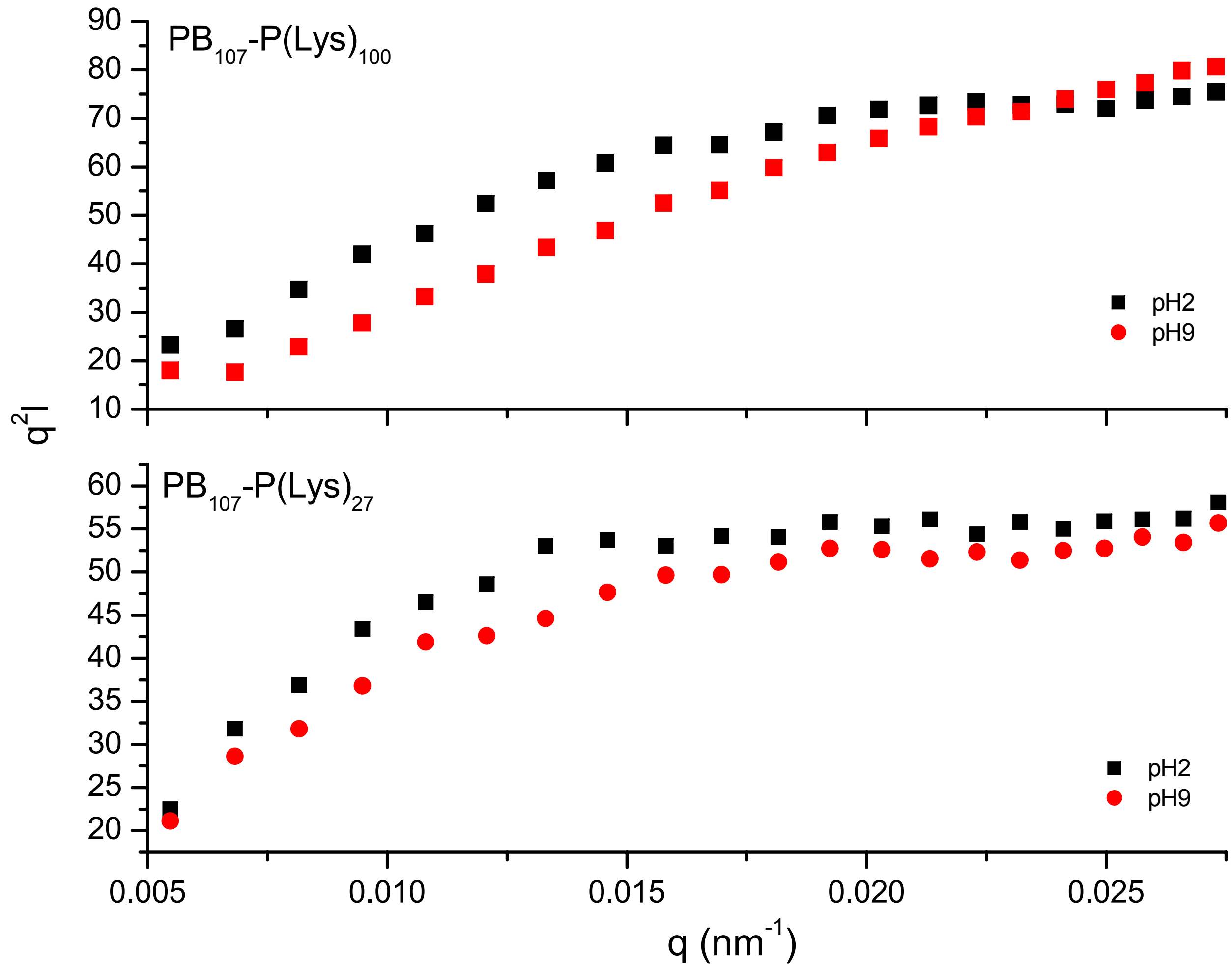
Note that hydrodynamic size is comparable to the PB_{107}-$P(Lys)_{27}$ system although the length of the P(Lys) chain is much longer

pH Response of 'Symmetric' PB_m-$P(Lys)_n$ from DLS



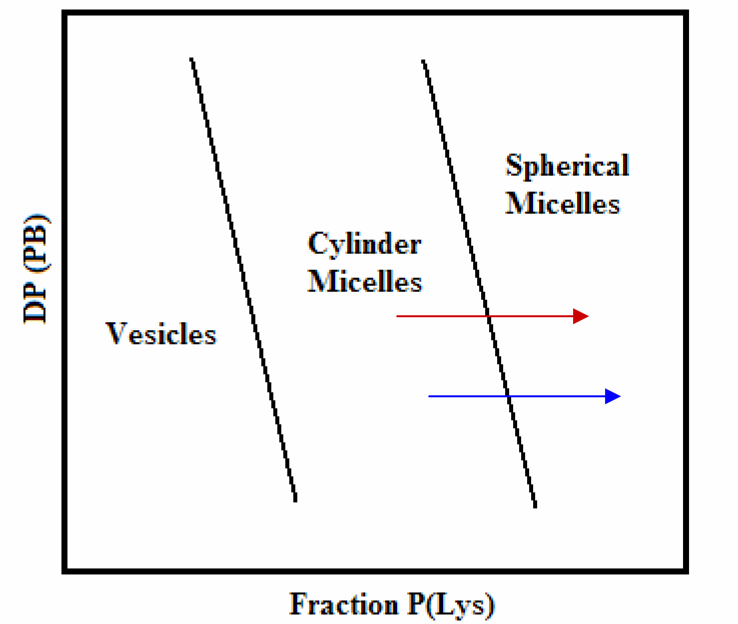
PB_{107}-$P(Lys)_{100}$
(scale = 200nm)

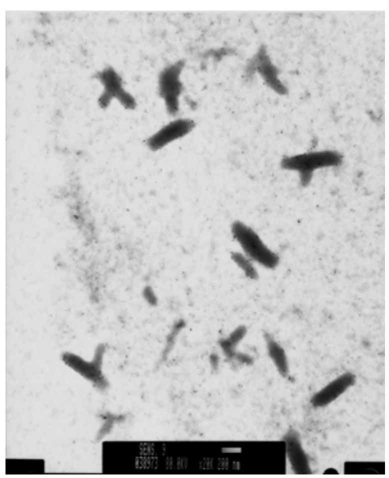
Kratky Plots



Static light scattering suggests a change in the form factor with pH for the PB_{107}-$P(Lys)_{100}$ sample, but not for the PB_{107}-$P(Lys)_{27}$ sample

Rice to Sphere Transition?

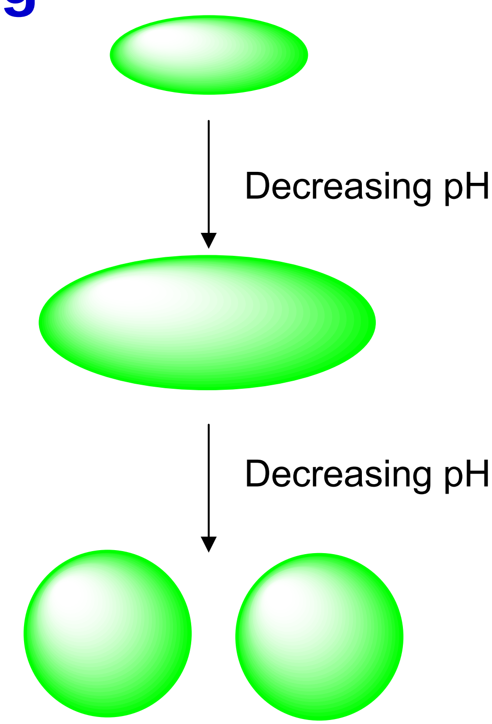




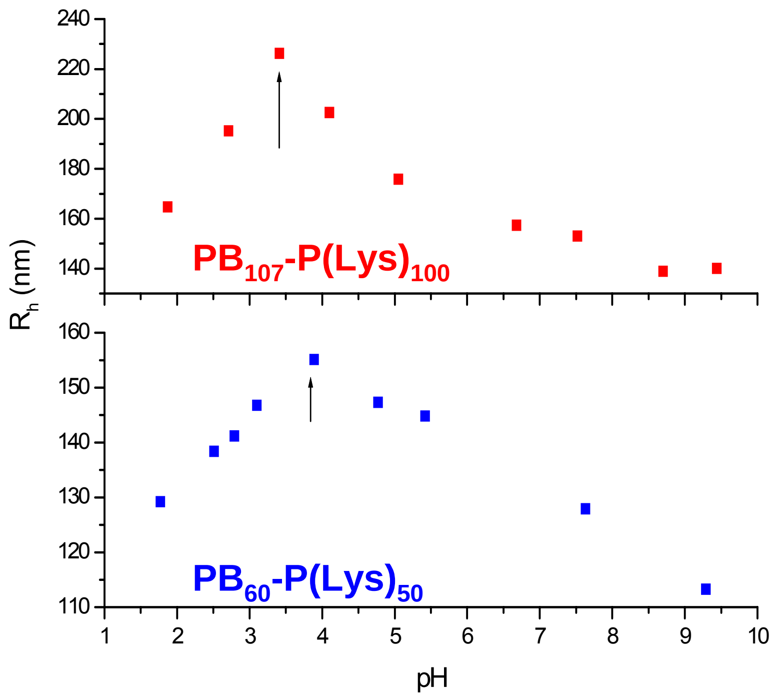
PB_{107}-$P(Lys)_{100}$
(scale = 200nm)

Possible Mechanism:

Budding



pH Response of 'Symmetric' Copolymers



- Position of the peak depends on P(Lys) block length

- pH response suggests rod-like micelles are swelling as pH is reduced
- At low pH, the micelle size peaks, then drops off with decreasing pH
- This drop is proposed to be a result of a morphological shift from rice-shaped micelles to spherical micelles
- This is consistent with that would happen if the effective fraction of the hydrophilic block were to increase

Future Directions

- Dual pH response:
  - Acid and basic chains
  - Triblock copolymers
- New hydrophobic blocks
- Dual temperature-pH responsive materials
- Incorporation of corona crosslinking sites
- Biocompatibility

Summary

- Light scattering is a powerful technique for characterization of polymeric materials in solution
- PB-P(Lys) block copolymers have been synthesized and show a rich diversity in morphology with varying composition
- Secondary structure changes within the P(Lys) corona chains induce response to solution conditions
- For PB-P(Lys), aggregate size and potentially morphology can change with solution pH and temperature

Funding:
UVM Startup

Vermont
EPSCoR

CD: Prof. Bruce Armitage (CMU)